An Integrated Approach for the Control of *Cryptosporidium parvum* Oocysts and Disinfection By-products in Drinking Water

Project Scope

Oocysts of the enteric protozoa *Cryptosporidium parvum* are often prevalent in surface waters used to produce drinking water. Unfortunately, these oocysts have a high resistance to inactivation with commonly used disinfectants such as free chlorine and monochloramine. Consequently, waterborne outbreaks of cryptosporidiosis resulting from ingestion of inadequately treated drinking water occur throughout the world, including the United States. Due to ineffectiveness of common disinfectants, many U.S. drinking water utilities have begun to use or are considering the use of ozone and chlorine dioxide to improve control of *C. parvum*, which is a central requirement of the proposed Long-Term 2 Enhanced Surface Water Treatment Rule. However, both of these strong oxidizing agents degrade rapidly by reacting with organic compounds commonly found in surface waters, forming disinfection by-products (DBPs)—which are also often of public health and regulatory concern and reduce the effectiveness of the disinfection process in controlling *Cryptosporidium*. Thus, many treatments plants that already use ozone or chlorine dioxide as a primary disinfectant also use free or combined chlorine as a secondary disinfectant in order to provide a residual in the distribution system as required by EPA's Stage 1 Disinfectants and Disinfection Byproducts Rule.

The overall goal of this project was the development of process design recommendations for the simultaneous control of *C. parvum* oocysts and DBPs (specifically bromate, formaldehyde, and cyanogen halides) in natural waters treated with ozone and chloramines. More specifically, the researchers sought to develop an integrated predictive model that would be calibrated with their experimental results and used to determine optimum process design. The model would also be verified in pilot- and full-scale water treatment systems. To carry out these objectives, the researchers conducted a series of laboratory, modeling, and field verification experiments over the course of the project.

Grant Title and Principal Investigators

Integrated Approach for the Control of *Cryptosporidium parvum* Oocysts and Disinfection By-Products in Drinking Water Treated with Ozone and Chloramines (EPA Grant #R826830)

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Key Findings and Implications

- Showed that the *C. parvum* oocyst inactivation rate with monochloramine after ozone pre-treatment was five times faster at 20ºC and 22 times faster at 1ºC than the corresponding rates of inactivation with monochloramine with no ozone pre-treatment; this has great implications for optimizing the control of pathogens and disinfection by-products (DBPs) for ozone/monochloramine sequential disinfection in colder regions.
- Developed a mechanistic predictive model that can be adapted to serve as a tool to predict both *C. parvum* inactivation and bromate formation in various ozone disinfection systems; it can be further adapted to simulate the inactivation of other pathogenic microorganisms by ozone disinfection systems and control of other types of DBPs.
- Elucidated mechanisms and developed an overall kinetic model for the formation of cyanogen bromide from monobromamine and formaldehyde, which may be used in future risk management actions to control cyanogen halides.

Publications include 8 peer reviewed journal articles and 15 conference/workshop presentations.

Project Period: September 1998 to March 2004

Relevance to ORD's *Drinking Water Research Multi-Year Plan* (2003 Edition)

This project contributes to two of Long-term Goals for drinking water research: (1) By 2010, develop scientifically sound data and approaches to assess and manage risks to human health posed by exposure to regulated waterborne pathogens and chemicals, including those addressed by the Arsenic, M/DBP, and Six-Year Review Rules; and (3) By 2009, provide data, tools and technologies to support management decisions by the Office of Water, state, local authorities and utilities to protect source water and the quality of water in the distribution system.

The results of this research provide a better understanding of the kinetics and interdependence or relationships between DBP formation/decomposition and *Cryptosporidium parvum* oocyst inactivation in water supply systems using ozone and chloramines as primary and secondary disinfectants, especially in cold water treatment conditions. For example, the research not only helped to elucidate mechanisms of the formation of the cyanogen bromide from monobromamine and formaldehyde (all DBPs), it also generated an overall kinetic model for their formation—all of which may be of future use regarding the control of cyanogen halides and other DBPs. The research also focused on controlling or treating water for *C. parvum*, which is a well known waterborne pathogen of both public health and regulatory concern. For example, its improved control in source waters for drinking water is a key component in the proposed Long-Term 2 Enhanced Surface Water Treatment Rule.

Project Results and Implications

<u>Synergistic Effects Associated With the Inactivation of *C. Parvum* Oocysts During Sequential Application of Ozone and Monochloramine</u>: Experiments on the inactivation kinetics of *C. parvum* oocysts with ozone and monochloramine used as single disinfectants were characterized by a lag phase during which little inactivation occurred, followed by pseudo-first order inactivation kinetics. The lag phase was found to increase and the rate of *C. parvum* inactivation to decrease as temperature decreased. The inactivation rates for both agents under all conditions were fit to an Arrhenius-type equation (describing the temperature-dependence of the inactivation) for the temperature range investigated of 1 to 20° C. The investigators then used this equation to predict inactivation kinetics at temperatures for which experimental data are not available. However, the researchers concluded that the inclusion of safety factors should be considered to account for the variability in oocyst resistance to disinfectant. The rate of *C. parvum* oocyst inactivation with monochloramine was enhanced when used as a secondary disinfectant to ozone and oocyst inactivation was found to increase as temperature decreased. Ozone pre-treatment also resulted in the abolition of the lag phase for monochloramine. The inactivation rate with monochloramine after ozone pre-treatment was five times faster at 20ºC and 22 times faster at 1ºC than the corresponding rates of inactivation with monochloramine when no ozone pre-treatment was applied. The researchers regard this as a very important finding, with important implications for optimizing the control of pathogens in regions where the water temperature may approach the freezing point.

<u>Integrated Models for the Simultaneous Prediction of *C. parvum* Inactivation and Bromate Formation</u>: The second area of research involved the development of integrated models for three ozone reactors having different hydrodynamic conditions: true batch; a bench-scale system with flow-through ozone bubble-diffuser contactor and external recirculation; and lab- and pilot-scale ozone bubble-diffuser contactors. The various models developed included the following key elements: (1) ozone decomposition kinetics and mechanism; (2) bromate formation mechanism; (3) *C. parvum* inactivation kinetics; (4) empirical estimation of ozone mass transfer; and (5) hydrodynamic conditions. The models were evaluated with experimental data and with pilot- and full-scale data obtained from water utilities. The mechanistic predictive model (MPM) for ozone decomposition and bromate formation—which incorporated more than 30 chemical species and more than 50 chemical reactions—was validated with data obtained from a batch ozone contactor operated with laboratory-prepared source waters. Experiments with a lab-scale flow-through ozone contactor with external recirculation were also

conducted with laboratory-prepared waters which were spiked with *C. parvum* oocysts to verify the integrated model for hydrodynamic conditions. The MPM was further refined by incorporating empirical data on the reactions of natural organic matter to simulate the bromate formation in natural water (i.e., treated Ohio River water). The model was evaluated with experimental data obtained with natural water in a batch reactor based on the concentrations of ozone, bromate, and a probe chemical *para*-dichlorobenzoic acid (pCBA), which was used to estimate time-integrated exposure to hydroxyl radical during ozonation. In all cases, semi-batch experiments were conducted to determine the inactivation kinetics of *C. parvum* oocyst, prior to the prediction of *C. parvum* inactivation levels in flow-through ozone contactors. Tracer tests were also performed with each reactor to confirm the validity of hydrodynamic models that were used for different ozone contactors. Figure 1 presents experimental results obtained from total flow-through reactor treatment corresponding to an applied ozone dose of 3.4 mg/L. It can be seen from Figure 1 that the model predictions for concentrations of dissolved ozone, pCBA, bromate, and *C. parvum* survival are consistent with the experimental data.

The MPM is expected to be a useful tool to predict both *C. parvum* inactivation and bromate formation in flow-through ozone bubble-diffuser contactors. Once the parameters that determine the kinetics of ozone decomposition, bromate formation, and *C. parvum* inactivation are determined from bench-scale batch and semi-batch tests, the model can be used to predict the performance in production-scale flow-through systems. The model can also be used to define optimal design criteria and operating conditions for ozone disinfection systems with respect to inactivation of *C. parvum* oocysts and control of bromate formation. Based on this research, the investigators developed several recommendations for the design and operation of ozone contactors to achieve both these goals. For example, source water pH has much greater impact than mixing conditions on bromate formation, while *C. parvum* inactivation does not depend on pH. Therefore, lowering the pH of the source water is a more efficient way to suppress the formation of

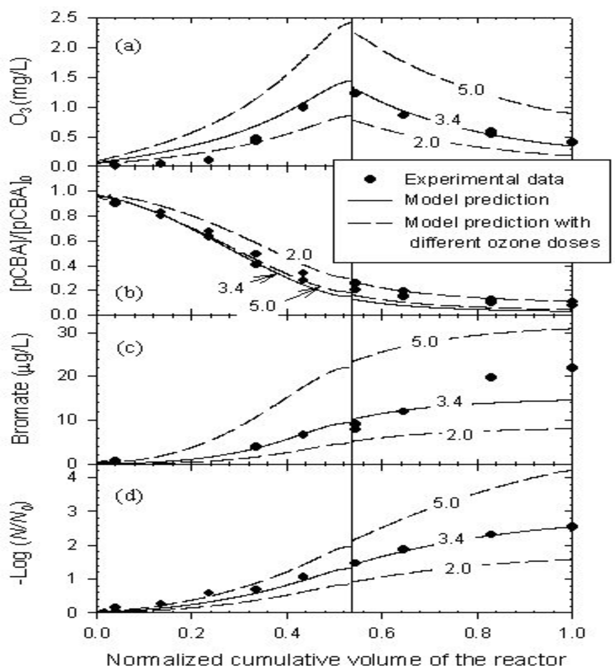

Figure 1. Comparison of profiles of (a) ozone concentration, (b) normalized pCBA concentration, (c) bromate concentration, and (d) survival ratio of *C. parvum* oocysts measured experimentally at ozone dose of 3.4 mg/L and predicted for different doses.

bromate than changing the hydrodynamic conditions of the existing water treatment process. The investigators warned however, that the effects of various operating and water quality parameters on the inactivation efficiency of *C. parvum* oocysts in pilot-scale ozone contactor should not be extended directly to other microorganisms, or to contactors with different design. They also cautioned against generalization of the model to other source waters and diffuser systems without additional bench-scale studies.

Ozone Disinfection and DBP Formation: Ozonation results in the formation of aldehydes, among which formaldehyde is typically formed at the highest concentration. Monochloramine and monobromamine formed in the presence of bromide can then react with formaldehyde undergoing a number of reactions that ultimately form cyanogen halides (e.g., cyanogen chloride and cyanogen bromide). The formation mechanism of cyanogen chloride from monochloramine and formaldehyde has been reported in the literature. The third and last phase of work conducted under this grant investigated a similar mechanism for the formation of cyanogen bromide from monobromamine and formaldehyde in two stages, the first involving bromamine decomposition and the second involving the reaction kinetics for bromamines and formaldehyde. Based on this research, the investigators developed a kinetic model to predict cyanogen bromide formation from the chain of reactions initiated by reaction between monobromamine and formaldehyde. This research and the model for cyanogen bromide formation provides information for future assessment of the control of cyanogen halides. For example, even though bromamine is not commonly applied as a disinfectant in drinking water treatment, conditions that favor the formation of bromamines (i.e., combined chlorine disinfection of bromide-containing waters) are often encountered, and formaldehyde is a common DBP in drinking water treated with various disinfectants, including ozone and combined chlorine.

Investigators

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For More Information

NCER Project Abstract and Reports:

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/207/report/0

Peer Reviewed Publications

Rennecker, J.L., Driedger, A.M., Rubin, S.A., and Mariňas, B.J. 2000. Synergy in sequential inactivation of *Cryptosporidium parvum* with ozone/free chlorine and ozone/monochloramine. Water Research 34(17): 4121-4130.

Rennecker, J.L., Corona-Vasquez, B., Driedger, A.M., and Mariňas, B.J. 2000. Synergisms in sequential disinfection of *Cryptosporidium parvum*. Water Science and Technology 41(7):47-52.

Driedger, A.M., Rennecker, J.L., and Mariňas, B.J. 2001. Inactivation of *Cryptosporidium parvum* oocysts with ozone and monochloramine at low temperature. Water Research 35(1): 41-48.

Rennecker, J.L., Corona-Vasquez, B., Driedger, A.M., Rubin, S.A., and Mariňas, B.J. 2001. Inactivation of *Cryptosporidium* parvum with sequential application of ozone and combined chlorine. Water Science and Technology 43(12):167-170.

Rennecker, J.L., Kim J.H., Corona-Vasquez, B., and Mariňas, B.J. 2001. Role of disinfectant concentration and pH in the inactivation kinetics of *Cryptosporidium parvum* oocysts with ozone and monochloramine. Environmental Science and Technology 35(13):2752-2757.

Kim J.-H,, Rennecker, J.L., Tomiakm R.B., Mariňas, B.J., Miltner, R.J., and Owens, J.H. 2002. Inactivation of *Cryptosporidium* oocysts in a pilot-scale bubble-diffuser contactor II: Model validation and application. ASCE Journal of Environmental Engineering 128(6):522-532.

Lei, H., Mariňas, B.J., Minear, R.A. 2004. Bromamine decomposition kinetics in aqueous solution. Environmental Science and Technology 38(7):2111-2119.

Kim, J.-H., von Gunten, U., Mariňas, B.J. 2004. Simultaneous prediction of *Cryptosporidium parvum* oocyst inactivation and bromate formation during ozonation of synthetic waters. Environmental Science and Technology 38(7):2232-2241.